09937274

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Priority 3/31/2000

3/31

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NEWS 1		Web Page URLs for STN Seminar Schedule - N. America
NEWS 2	Apr 08	"Ask CAS" for self-help around the clock
NEWS 3	Apr 09	BEILSTEIN: Reload and Implementation of a New Subject Area
NEWS 4	Apr 09	ZDB will be removed from STN
NEWS 5	Apr 19	US Patent Applications available in IFICDB, IFIPAT, and IFIUDB
NEWS 6	Apr 22	Records from IP.com available in CAPLUS, HCAPLUS, and ZCAPLUS
NEWS 7	Apr 22	BIOSIS Gene Names now available in TOXCENTER
NEWS 8	Apr 22	Federal Research in Progress (FEDRIP) now available
NEWS 9	Jun 03	New e-mail delivery for search results now available
NEWS 10	Jun 10	MEDLINE Reload
NEWS 11	Jun 10	PCTFULL has been reloaded
NEWS 12	Jul 02	FOREGE no longer contains STANDARDS file segment
NEWS 13	Jul 22	USAN to be reloaded July 28, 2002; saved answer sets no longer valid
NEWS 14	Jul 29	Enhanced polymer searching in REGISTRY
NEWS 15	Jul 30	NETFIRST to be removed from STN
NEWS 16	Aug 08	CANCERLIT reload
NEWS 17	Aug 08	PHARMAMarketLetter(PHARMAML) - new on STN
NEWS 18	Aug 08	NTIS has been reloaded and enhanced
NEWS 19	Aug 19	Aquatic Toxicity Information Retrieval (AQUIRE) now available on STN
NEWS 20	Aug 19	IFIPAT, IFICDB, and IFIUDB have been reloaded
NEWS 21	Aug 19	The MEDLINE file segment of TOXCENTER has been reloaded
NEWS 22	Aug 26	Sequence searching in REGISTRY enhanced
NEWS 23	Sep 03	JAPIO has been reloaded and enhanced
NEWS 24	Sep 16	Experimental properties added to the REGISTRY file
NEWS 25	Sep 16	CA Section Thesaurus available in CAPLUS and CA
NEWS 26	Oct 01	CASREACT Enriched with Reactions from 1907 to 1985
NEWS 27	Oct 21	EVENTLINE has been reloaded
NEWS 28	Oct 24	BEILSTEIN adds new search fields
NEWS 29	Oct 24	Nutraceuticals International (NUTRACEUT) now available on STN
NEWS 30	Oct 25	MEDLINE SDI run of October 8, 2002
NEWS 31	Nov 18	DKILIT has been renamed APOLLIT
NEWS 32	Nov 25	More calculated properties added to REGISTRY
NEWS 33	Dec 02	TIBKAT will be removed from STN
NEWS 34	Dec 04	CSA files on STN
NEWS 35	Dec 17	PCTFULL now covers WP/PCT Applications from 1978 to date
NEWS 36	Dec 17	TOXCENTER enhanced with additional content
NEWS 37	Dec 17	Adis Clinical Trials Insight now available on STN
NEWS 38	Dec 30	ISMEC no longer available
NEWS 39	Jan 13	Indexing added to some pre-1967 records in CA/CAPLUS
NEWS 40	Jan 21	NUTRACEUT offering one free connect hour in February 2003
NEWS 41	Jan 21	PHARMAML offering one free connect hour in February 2003

NEWS EXPRESS January 6 CURRENT WINDOWS VERSION IS V6.01a,
CURRENT MACINTOSH VERSION IS V6.0b(ENG) AND V6.0Jb(JP),

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                AND CURRENT DISCOVER FILE IS DATED 01 OCTOBER 2002
 NEWS HOURS     STN Operating Hours Plus Help Desk Availability
 NEWS INTER     General Internet Information
 NEWS LOGIN     Welcome Banner and News Items
 NEWS PHONE     Direct Dial and Telecommunication Network Access to STN
 NEWS WWW       CAS World Wide Web Site (general information)

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FILE 'HOME' ENTERED AT 12:37:05 ON 25 JAN 2003

=> file reg
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                       0.21       0.21

FILE 'REGISTRY' ENTERED AT 12:37:38 ON 25 JAN 2003
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STRUCTURE FILE UPDATES:   24 JAN 2003  HIGHEST RN 481628-73-3
DICTIONARY FILE UPDATES:  24 JAN 2003  HIGHEST RN 481628-73-3

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

  Please note that search-term pricing does apply when
  conducting SmartSELECT searches.

Crossover limits have been increased.  See HELP CROSSOVER for details.

Experimental and calculated property data are now available.  See HELP
PROPERTIES for more information.  See STNote 27, Searching Properties
in the CAS Registry File, for complete details:
http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

=> s 19-nir testosterone
        235470 19
            78 NIR
          1208 TESTOSTERONE
L1           0 19-NIR TESTOSTERONE
                 (19(W)NIR(W)TESTOSTERONE)

=> s 19-nor testosterone
```

```
        235470 19
        152302 NOR
          1208 TESTOSTERONE
L2         162 19-NOR TESTOSTERONE
               (19(W)NOR(W)TESTOSTERONE)

=> s l2 7-substituted
MISSING OPERATOR

=> s l2 and 7-substituted
       2961735 7
           884 SUBSTITUTED
             0 7-SUBSTITUTED
                 (7(W)SUBSTITUTED)
L3           0 L2 AND 7-SUBSTITUTED

=> file caplus
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                      34.56      34.77

FILE 'CAPLUS' ENTERED AT 12:38:52 ON 25 JAN 2003
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FILE COVERS 1907 - 25 Jan 2003  VOL 138 ISS 5
FILE LAST UPDATED: 24 Jan 2003  (20030124/ED)

  This file contains CAS Registry Numbers for easy and accurate
  substance identification.


=> d his

     (FILE 'HOME' ENTERED AT 12:37:05 ON 25 JAN 2003)

     FILE 'REGISTRY' ENTERED AT 12:37:38 ON 25 JAN 2003
L1             0 S 19-NIR TESTOSTERONE
L2           162 S 19-NOR TESTOSTERONE
L3             0 S L2 AND 7-SUBSTITUTED

     FILE 'CAPLUS' ENTERED AT 12:38:52 ON 25 JAN 2003

=> s l2 and 7-alkyl
          6755 L2
       2305927 7
        500431 ALKYL
```

```
          1966 7-ALKYL
                 (7(W)ALKYL)
L4           3 L2 AND 7-ALKYL

=> s l2 and 7 methyl
          6755 L2
       2305927 7
        778688 METHYL
          6873 7 METHYL
                 (7(W)METHYL)
L5          13 L2 AND 7 METHYL

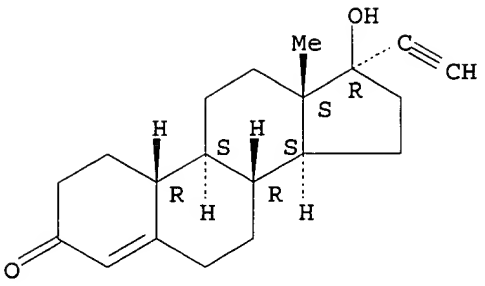
=> s l2 and 7ethyl
          6755 L2
             4 7ETHYL
L6           0 L2 AND 7ETHYL

=> s l2 and 7 ethyl
          6755 L2
       2305927 7
        330054 ETHYL
          1319 7 ETHYL
                 (7(W)ETHYL)
L7           1 L2 AND 7 ETHYL

=> d l7 ibib hitstr abs

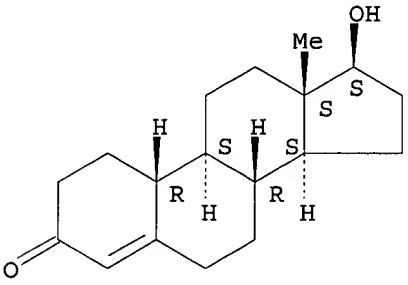
L7   ANSWER 1 OF 1  CAPLUS  COPYRIGHT 2003 ACS
ACCESSION NUMBER:         1978:2304  CAPLUS
DOCUMENT NUMBER:          88:2304
TITLE:                    Interaction of steroids with Pseudomonas testosteroni
                          3-oxosteroid .DELTA.4-.DELTA.5-isomerase
AUTHOR(S):                Weintraub, Hadassa; Vincent, Francoise; Baulieu,
                          Etienne Emile; Alfsen, Annette
CORPORATE SOURCE:         Unite Rech. Metab. Mol. Physiopathol. Steroides,
                          INSERM, Bicetre, Fr.
SOURCE:                   Biochemistry (1977), 16(23), 5045-53
                          CODEN: BICHAW; ISSN: 0006-2960
DOCUMENT TYPE:            Journal
LANGUAGE:                 English
IT   68-22-4 434-22-0 514-61-4 793-55-5
     797-63-7 1425-10-1 3764-87-2 4811-77-2
     6218-29-7 10161-33-8
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (reaction of, with steroid .DELTA.-isomerase, structure in relation to)
RN   68-22-4  CAPLUS
CN   19-Norpregn-4-en-20-yn-3-one, 17-hydroxy-, (17.alpha.)- (9CI)  (CA INDEX
     NAME)

Absolute stereochemistry.
```



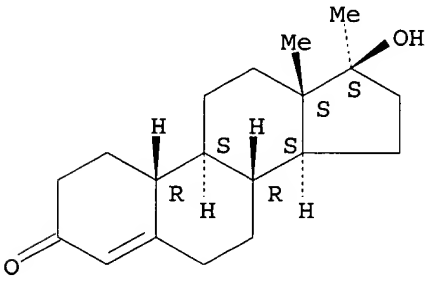
RN 434-22-0 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



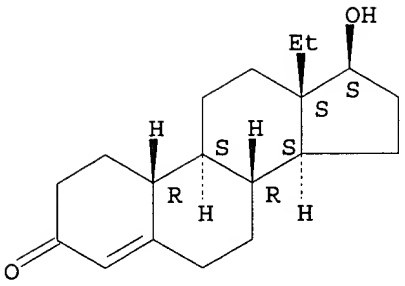
RN 514-61-4 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-17-methyl-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



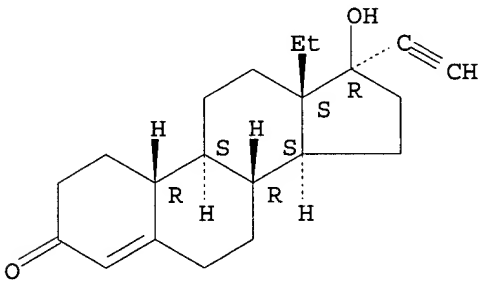
RN 793-55-5 CAPLUS
CN Gon-4-en-3-one, 13-ethyl-17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



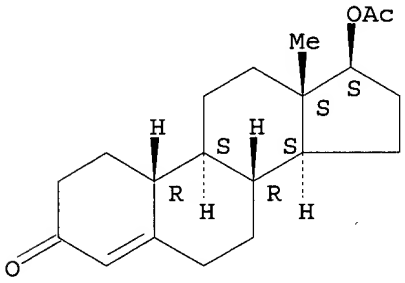
RN 797-63-7 CAPLUS
CN 18,19-Dinorpregn-4-en-20-yn-3-one, 13-ethyl-17-hydroxy-, (17.alpha.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



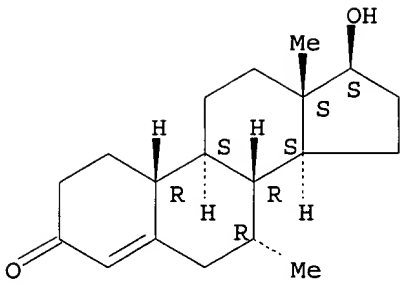
RN 1425-10-1 CAPLUS
CN Estr-4-en-3-one, 17-(acetyloxy)-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



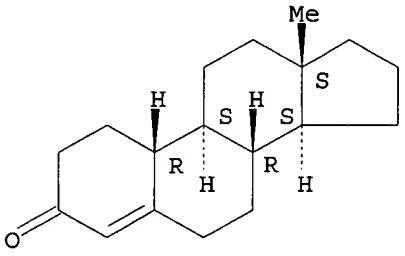
RN 3764-87-2 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



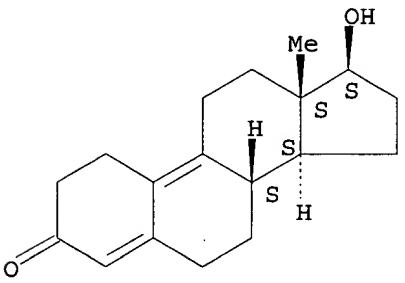
RN 4811-77-2 CAPLUS
CN Estr-4-en-3-one (7CI, 8CI, 9CI) (CA INDEX NAME)

Absolute stereochemistry.



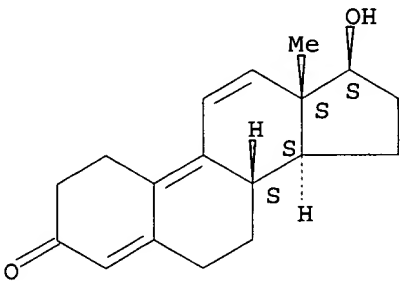
RN 6218-29-7 CAPLUS
CN Estra-4,9-dien-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 10161-33-8 CAPLUS
CN Estra-4,9,11-trien-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



AB The structural features of a no. of steroids and synthetic derivs. were related to their potency as competitive or noncompetitive inhibitors of the isomerization of 5-androstene-3,17-dione by P. testosteroni 3-oxosteroid .DELTA.4-.DELTA.5-isomerase (I). Any substituent introduced at the C-11 (.alpha. or .beta.) position of C18, C19, and C21 steroids hinders the interaction with I. With phenolic C18 derivs., the C-3 hydroxyl is essential for firm interaction; removal or replacement of this group by a Me or methoxy group weakens binding. The absence of a substituent at the C-17.beta. position or the lengthening of the C-17.beta. side chain increases the affinity of both C18 and C19 steroids. With C19 and C21 steroids, the absence of the angular C-19 Me group as well as the presence of a conjugated double bond system at C-9 or C-9 and C-11 favors binding. Substituents introduced at the C-13 and C-17.alpha. positions have different effects on phenolic steroids and 3-oxo-.DELTA.4 derivs. Lengthening the C-18 hydrocarbon side chain increases markedly the affinity of 3-oxo-.DELTA.4-monounsatd. steroids, but does not affect binding of phenolic steroids. This affinity increase is less pronounced with polyunsatd. C18.DELTA.4,9,11 derivs. (with 17.alpha.-substituents). The presence of a Me, hydroxyl, ethynyl, or acetoxy group at C-17.alpha. markedly decreases the affinity of 3-oxo-.DELTA.4-C19 and C21 derivs., but not of phenolic steroids. Apparently, the fit of rings C and D in the binding site of I differs for 3-oxo-.DELTA.4 and phenolic derivs. Some ligands, which are structurally similar to competitive inhibitors, exhibit pure noncompetitive or mixed noncompetitive behavior. Estradiol is a competitive inhibitor, whereas estrone and its derivs. are noncompetitive. Diethylstilbestrol and the 4,4'-dihydroxy-2',7-dimethyl-**7**'-**ethyl**-trans-stilbene are competitive, whereas 4,4'-dihydroxy-2',7'-dimethyl-**7**-**ethyl**-trans-stilbene is a noncompetitive inhibitor. 3-Deoxyestradiol and coumestrol are mixed noncompetitive inhibitors. The affinities of estradiol and estrone for I show the same pH dependence, and equil. dialysis studies suggest that estrone and estradiol compete for the same binding site of I. These findings complement the previously reported half-of-sites reactivity of the I dimetric protein, and suggest that a flip-flop mechanism may be involved.

=>
=> d his

(FILE 'HOME' ENTERED AT 12:37:05 ON 25 JAN 2003)

FILE 'REGISTRY' ENTERED AT 12:37:38 ON 25 JAN 2003
L1 0 S 19-NIR TESTOSTERONE
L2 162 S 19-NOR TESTOSTERONE
L3 0 S L2 AND 7-SUBSTITUTED

FILE 'CAPLUS' ENTERED AT 12:38:52 ON 25 JAN 2003

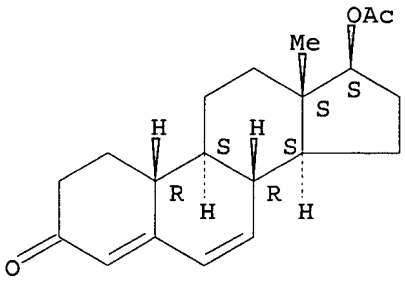
09937274

L4 3 S L2 AND 7-ALKYL
L5 13 S L2 AND 7 METHYL
L6 0 S L2 AND 7ETHYL
L7 1 S L2 AND 7 ETHYL

=> d l4 1-3 ibib hitstr abs

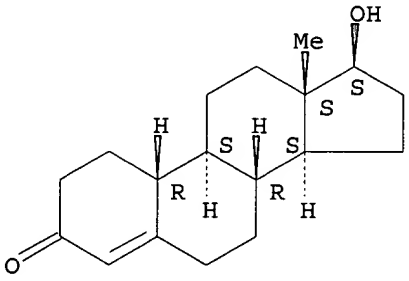
L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1976:524227 CAPLUS
DOCUMENT NUMBER: 85:124227
TITLE: Antiprogestational agents. The synthesis of 7 -**alkyl** steroidal ketones with anti-implantational and antidecidual activity
AUTHOR(S): Grunwell, Joyce F.; Benson, Harvey D.; Johnston, J. O'Neal; Petrow, Vladimir
CORPORATE SOURCE: Div. Richardson-Merrell Inc., Merrell-Natl. Lab., Cincinnati, OH, USA
SOURCE: Steroids (1976), 27(6), 759-71
CODEN: STEDAM; ISSN: 0039-128X
DOCUMENT TYPE: Journal
LANGUAGE: English
IT **2590-41-2**
RL: RCT (Reactant); RACT (Reactant or reagent)
(addn. reaction of, with alkyl copper compds.)
RN 2590-41-2 CAPLUS
CN Estra-4,6-dien-3-one, 17-(acetyloxy)-, (17.beta.)- (9CI) (CA INDEX NAME)

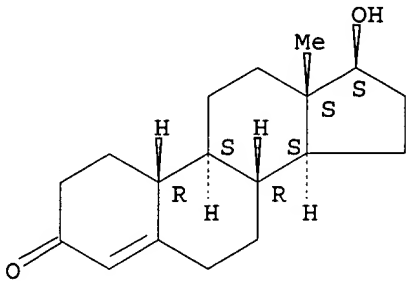
Absolute stereochemistry.



IT **434-22-0**
RL: RCT (Reactant); RACT (Reactant or reagent)
(enol acetylation of)
RN 434-22-0 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

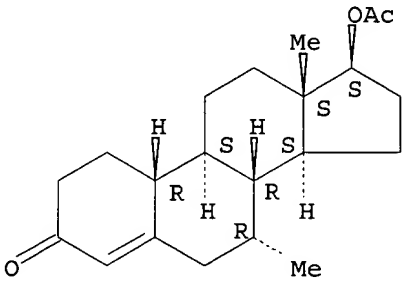
Absolute stereochemistry.



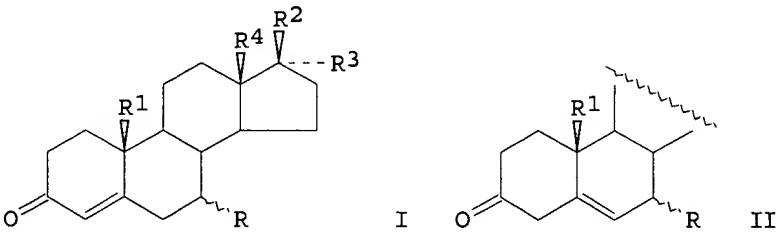


IT **6157-87-5P**
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)
(prepn. and antifertility activity of)
RN 6157-87-5 CAPLUS
CN Estr-4-en-3-one, 17-(acetyloxy)-7-methyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



GI



AB Oxo unsatd. steroids I and II (R = alkyl, R1 = H, Me; R2 = OH, OAc; R3 = H, Me, C.tplbond.CH; R2R3 = O; R4 = Me, Et) (28 compds.) were prepd. by 1,6-conjugate addn. of organocopper reagents to the corresponding 3-oxo 4,6-unsatd. androstanes, estranes, and gonanes. I and II (R = .alpha.-Me, R1 = R3 = H, R2 = OAc, R4 = Me) and II (R = .alpha.-Me, R1 = Me, R2 = OH, R3 = R4 = Me) had significant anti-implantational and antidecidual activities. The contragestative effects were assocd. with the latter antihormonal properties, and not with the androgenicity of these compds.

L4 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2003 ACS

09937274

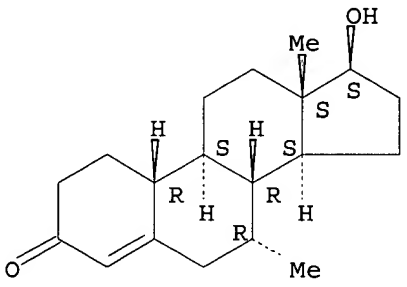
ACCESSION NUMBER: 1975:579399 CAPLUS
DOCUMENT NUMBER: 83:179399
TITLE: **7-Alkyl**-.DELTA.3,5-steroids
INVENTOR(S): Grunwell, Joyce F.; Johnston, John O.; Petrow, Vladimir; Weintraub, Philip M.
PATENT ASSIGNEE(S): Richardson-Merrell Inc., USA
SOURCE: U.S., 12 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3890356	A	19750617	US 1973-344838	19730326
ZA 7400932	A	19750129	ZA 1974-932	19740212
AU 7465584	A1	19750814	AU 1974-65584	19740214
JP 49126661	A2	19741204	JP 1974-28209	19740313
GB 1410294	A	19751015	GB 1974-12368	19740320
DE 2413559	A1	19741017	DE 1974-2413559	19740321
FR 2223014	A1	19741025	FR 1974-9975	19740322
BE 812836	A1	19740715	BE 1974-142453	19740326

PRIORITY APPLN. INFO.: US 1973-344838 19730326

IT **3764-87-2**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction with methyl lithium)
RN 3764-87-2 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



GI For diagram(s), see printed CA Issue.
AB The antiprogestational and contraceptive androstadienes I (R = Ph, Bu, Me) were prepd. by condensation of 7.alpha.-methyltestosterone with PhMgCl, BuLi, and MeLi, resp., and subsequent acid catalyzed dehydration. 3,7.alpha.-Dimethylestra-3,5-dien-17.beta.-ol acetate, 7.alpha.-methyl-3-phenylestra-3,5-dien-17.beta.-ol, 3,4,7.alpha.-trimethylandrosta-3,5-dien-17.beta.-ol, 7.alpha.-methylandrosta-3,5-dien-17.beta.-ol, 3,7.alpha.-dimethylandrosta-3,5-diene-11.beta.,17.beta.-diol, and 1.alpha.,3,7.alpha.-trimethylandrosta-3,5-dien-17.beta.-ol were prepd. similarly.

L4 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1974:27434 CAPLUS
DOCUMENT NUMBER: 80:27434

09937274

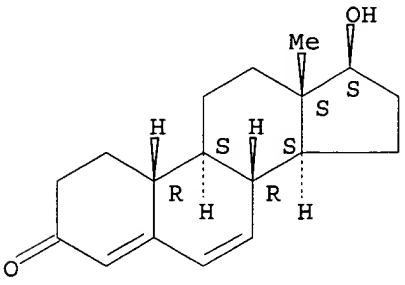
TITLE: 3-Oxo-7-**alkyl**-.DELTA.5-steroids
INVENTOR(S): Grunwell, Joyce F.; Benson, Harvey D.; Petrow, Vladimir
PATENT ASSIGNEE(S): Richardson-Merrell Inc.
SOURCE: Ger. Offen., 67 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2309328	A1	19731004	DE 1973-2309328	19730224
US 3833621	A	19740903	US 1972-236186	19720320
ZA 7300718	A	19731031	ZA 1973-718	19730131
AU 7351971	A1	19740808	AU 1973-51971	19730208
CA 1004667	A1	19770201	CA 1973-163914	19730216
GB 1416277	A	19751203	GB 1973-8774	19730222
NL 7302540	A	19730924	NL 1973-2540	19730223
CH 586236	A	19770331	CH 1973-3048	19730301
JP 49011870	A2	19740201	JP 1973-27642	19730310
BE 796909	A1	19730716	BE 1973-128910	19730316
SE 406591	C	19790531	SE 1973-3850	19730319
SE 406591	B	19790219		
FR 2181834	A1	19731207	FR 1973-9992	19730320

PRIORITY APPLN. INFO.: US 1972-236186 19720320

IT **14531-84-1**
RL: RCT (Reactant); RACT (Reactant or reagent)
(methylation of)
RN 14531-84-1 CAPLUS
CN Estra-4,6-dien-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



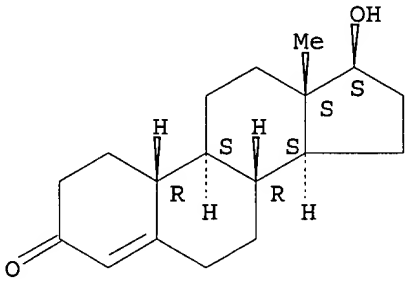
GI For diagram(s), see printed CA Issue.
AB Androstenones I (R =.alpha.-Me, .beta.-Me, .beta.-Me2CH; R1 = HO, AcO, EtCO2, Ac; R2 = H, Me, C.tplbond.CH; R1R2 = O, OCH2CH2O) (13 compds.), possessing anabolic, androgenic, progestational, and fertility inhibiting activity, were prepd. by reaction of LiR2Cu with the corresponding androstadienones II. Isomerization of I (R = .alpha.-Me, R1 = HO, R2 = H) with NaOMe in MeOH gave the corresponding .DELTA.4-isomer, which was used in treatment of prostate gland hypertrophy.

=> d l5 1-13 ibib hitstr abs

09937274

L5 ANSWER 1 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2001:8035 CAPLUS
DOCUMENT NUMBER: 137:63379
TITLE: Synthesis of (3.alpha.,7.beta.,17.alpha.)-7-**methyl**-19-norpregn-5(10)-en-20-yne-3,7,17-triol, a metabolite of ORG OD14, and its 7-epimer. [Erratum to document cited in CA133:362880]
AUTHOR(S): Plate, R.; van Wuijtswinkel, R. C. A. L.; Jans, C. G. J. M.; Groen, M. B.
CORPORATE SOURCE: Medicinal Chemistry Department, N.V. Organon, Oss, 5340, Neth.
SOURCE: Steroids (2001), 66(2), 115,117-126
CODEN: STEDAM; ISSN: 0039-128X
PUBLISHER: Elsevier Science Inc.
DOCUMENT TYPE: Journal
LANGUAGE: English
IT **434-22-0**, 19-NorTestosterone
RL: RCT (Reactant); RACT (Reactant or reagent)
(synthesis of (3.alpha.,7.beta.,17.alpha.)-**7-methyl**-19-norpregn-5(10)-en-20-yne-3, 7,17-triol metabolite of ORG OD14 and its 7-epimer (Erratum))
RN 434-22-0 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



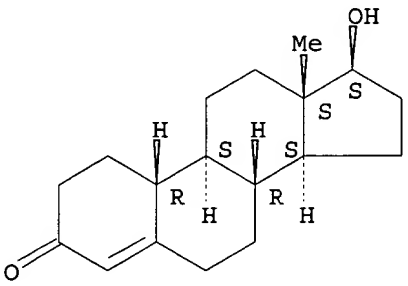
AB The Schemes in the article were not printed; the correct version of the article is given.
REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2000:620309 CAPLUS
DOCUMENT NUMBER: 133:362880
TITLE: Synthesis of (3.alpha.,7.beta.,17.alpha.)-7-**methyl**-19-norpregn-5(10)-en-20-yne-3,7,17-triol, a metabolite of ORG OD14, and its 7-epimer
AUTHOR(S): Plate, R.; van Wuijtswinkel, R. C. A. L.; Jans, C. G. J. M.; Groen, M. B.
CORPORATE SOURCE: Medicinal Chemistry Department, N.V. Organon, Oss, 5340, Neth.
SOURCE: Steroids (2000), 65(9), 497-504
CODEN: STEDAM; ISSN: 0039-128X
PUBLISHER: Elsevier Science Inc.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 133:362880

09937274

IT **434-22-0**, 19-NorTestosterone
RL: RCT (Reactant); RACT (Reactant or reagent)
(synthesis of (3.alpha.,7.beta.,17.alpha.)-**7-methyl**
-19-norpregn-5(10)-en-20-yne-3,7,17-triol, a metabolite of ORG OD14,
and its 7-epimer)
RN 434-22-0 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



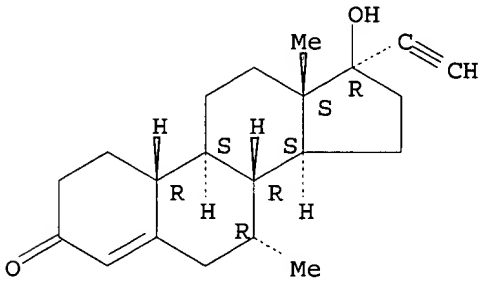
AB The syntheses of the 7.beta.-hydroxy metabolite of ORG OD14 (Livial.RTM.), (3.alpha.,7.beta.,17.alpha.)-**7-methyl**
-19-norpregn-5(10)-en-20-yne-3,7,17-triol, and its 7-epimer, (3.alpha.,7.alpha.,17.alpha.)-**7-methyl**
-19-norpregn-5(10)-en-20-yne-3,7,17-triol, are described.
REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 2000:277997 CAPLUS
DOCUMENT NUMBER: 132:308546
TITLE: High purity composition of (7.alpha.,17.alpha.)-17-hydroxy-**7-methyl**
-19-nor-17-pregn-5(10)-en-20-yn-3-one
INVENTOR(S): Kirchholtes, Peter Huub Gerard Maria; Sas, Gerard Arnoud Jozef Maria Theresia
PATENT ASSIGNEE(S): Akzo Nobel N. V., Neth.
SOURCE: PCT Int. Appl., 19 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2000023460	A1	20000427	WO 1999-EP7768	19991011
W: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
CA 2344686	AA	20000427	CA 1999-2344686	19991011
AU 9962029	A1	20000508	AU 1999-62029	19991011
BR 9914441	A	20010626	BR 1999-14441	19991011

EP 1121375 A1 20010808 EP 1999-948994 19991011
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO
JP 2002527525 T2 20020827 JP 2000-577186 19991011
EP 1275379 A2 20030115 EP 2002-22689 19991011
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI, CY
NO 2001001664 A 20010403 NO 2001-1664 20010403
PRIORITY APPLN. INFO.: EP 1998-203460 A 19981016
EP 1999-948994 A3 19991011
WO 1999-EP7768 W 19991011
OTHER SOURCE(S): CASREACT 132:308546
IT **1162-60-3P**, Org om38
RL: BYP (Byproduct); IMF (Industrial manufacture); PREP (Preparation)
(high purity compn. of (7.alpha.,17.alpha.)-17-hydroxy-**7-methyl**-19-nor-17-pregn-5(10)-en-20-yn-3-one)
RN 1162-60-3 CAPLUS
CN 19-Norpregn-4-en-20-yn-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.alpha.)-(9CI) (CA INDEX NAME)

Absolute stereochemistry.



AB The invention pertains to a process for the prepn. of a high purity (7.alpha.,17.alpha.)-17-hydroxy-**7-methyl**-19-nor-17-pregn-5(10)-en-20-yn-3-one (Tibolone)(I). The process provides for a compn. with less than 0.5 % of (7.alpha.,17.alpha.)-17-hydroxy-**7-methyl**-19-nor-17-pregn-4-en-20-yn-3-one (II). Thus, (7.alpha.,17.alpha.)-3,3-dimethoxy-17-hydroxy-**7-methyl**-19-nor-17-pregn-5(10)-en-20-yn-3-one in pyridine and ethanol was treated with oxalic acid in water to give I contg. less than 0.1% II. I can be used as a source for the prepn. of stable pharmaceutical dosage units. The stability of I in tablets was detd. after storage.
REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 4 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1999:819397 CAPLUS
DOCUMENT NUMBER: 132:50158
TITLE: Preparation of (7.alpha.,17.beta.)-**7-methyl**-17-[(1-oxoundecyl)oxy]estr-4-en-3-one
INVENTOR(S): Leysen, Dirk; Van der Voort, Hendrikus Adrianus Antonius
PATENT ASSIGNEE(S): Akzo Nobel N.V., Neth.
SOURCE: PCT Int. Appl., 13 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9967271	A1	19991229	WO 1999-EP4102	19990614
W: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
CA 2333985	AA	19991229	CA 1999-2333985	19990614
AU 9946101	A1	20000110	AU 1999-46101	19990614
BR 9911344	A	20010313	BR 1999-11344	19990614
EP 1087986	A1	20010404	EP 1999-929208	19990614
EP 1087986	B1	20020410		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
AT 215961	E	20020415	AT 1999-929208	19990614
JP 2002518514	T2	20020625	JP 2000-555922	19990614
ES 2175989	T3	20021116	ES 1999-929208	19990614
NO 2000006455	A	20001218	NO 2000-6455	20001218
US 6437158	B1	20020820	US 2000-719927	20001218

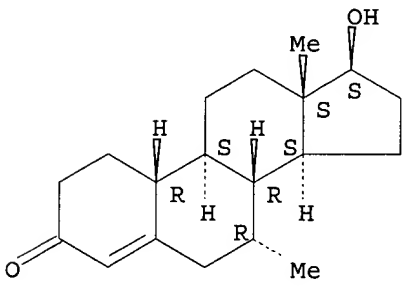
PRIORITY APPLN. INFO.: EP 1998-202052 A 19980619
WO 1999-EP4102 W 19990614

IT **3764-87-2**, 17.beta.-Hydroxy-7.alpha.-methylestr-4-en-3-one
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of (7.alpha.,17.beta.)-**7-methyl**-17-(undecanoyloxy)estr-4-en-3-one as a sol. androgen)

RN 3764-87-2 CAPLUS

CN Estr-4-en-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



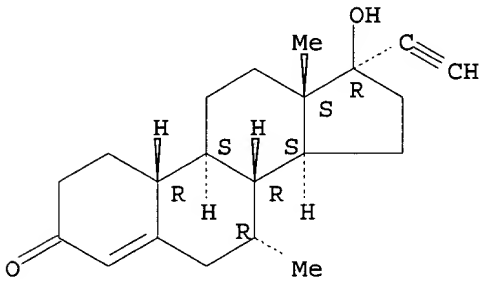
AB The invention is the novel androgen (7.alpha.,17.beta.)-**7-methyl**-17-[(1-oxoundecyl)oxy]estr-4-en-3-one (MENT undecanoate). This compd. distinguishes favorably from other testosterone derivs. in that it has a good soly. in oily media. It particularly exhibits a good dissolved potency relative to testosterone. The compd. is particularly suitable for administration by means of injection. Thus, MENT undecanoate was prepd. from 17.beta.-hydroxy-7.alpha.-methylestr-4-en-3-one and undecanoyl chloride. The relative dissolved potency (RDP) of MENT undecanoate was > 200 compared to testosterone.

REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS

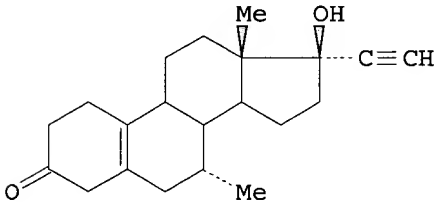
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 5 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1987:629374 CAPLUS
DOCUMENT NUMBER: 107:229374
TITLE: Pharmacological studies with (7.alpha.,17.alpha.)-17-hydroxy-**7-methyl**-19-norpregn-5(10)-en-20-yn-3-one (Org OD 14)
AUTHOR(S): Van der Vies, J.
CORPORATE SOURCE: Biochem. Pharmacol. Res., Organon Int. B. V., Oss, 5340 BH, Neth.
SOURCE: Maturitas (1987), Suppl. 1, 15-24
CODEN: MATUDK; ISSN: 0378-5122
DOCUMENT TYPE: Journal
LANGUAGE: English
IT **1162-60-3**
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); BIOL (Biological study)
(as Org OD 14 metabolite, biol. activities of)
RN 1162-60-3 CAPLUS
CN 19-Norpregn-4-en-20-yn-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.alpha.)-(9CI) (CA INDEX NAME)

Absolute stereochemistry.



GI

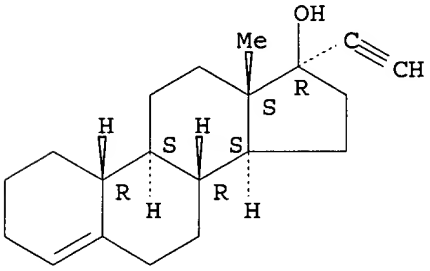


I

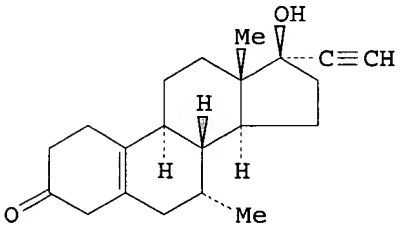
AB Hormonal screening studies in rats and rabbits indicated that Org OD 14 (I) had concomitant weak estrogenic, androgenic, and progestational activities. The effects obsd. in other tests, i.e., inhibition of ovulation in rats, prevention of bone loss following ovariectomy in rats, and restoration of sex drive in castrated male rats, corresponded to this hormonal profile. Studies of the metabolites of I in rats suggested that these are involved in the complex endocrinol. properties displayed by the compd.

L5 ANSWER 6 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1984:417625 CAPLUS
DOCUMENT NUMBER: 101:17625
TITLE: Multicenter study of effects of Org OD 14 on endometrium, vaginal cytology and cervical mucus in post-menopausal and oophorectomized women
AUTHOR(S): Punnonen, R.; Liukko, P.; Cortex-Prieto, J.; Eydam, F.; Milojevic, S.; Trevoux, R.; Chryssikopoulos, E.; Franchi, F.; Luisi, M.; Kicovic, P. M.
CORPORATE SOURCE: Dep. Gynaecol. Obstetr., Univ. Turku, Turku, Finland
SOURCE: Maturitas (1984), 5(4), 281-6
CODEN: MATUDK; ISSN: 0378-5122
DOCUMENT TYPE: Journal
LANGUAGE: English
IT **52-76-6**
RL: BIOL (Biological study)
(uterus and vagina response to withdrawal of synthetic steroid and, in postmenopausal women)
RN 52-76-6 CAPLUS
CN 19-Norpregn-4-en-20-yn-17-ol, (17.alpha.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



GI



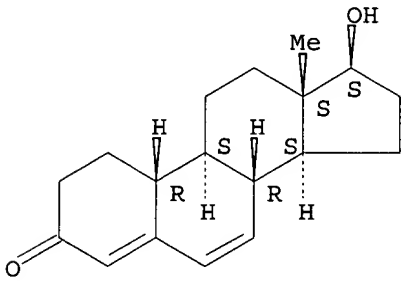
I

AB A study of 69 post-menopausal or oophorectomized women was performed to det. whether Org OD 14 [(7.alpha.,17.alpha.)-17-hydroxy-7-**methyl**-19-norpregn-5(10)-en-20-yn-3-one](I) [5630-53-5] administered orally in a daily dose of 2.5 mg for 90 days induces endometrial proliferation. The treatment with Org OD 14 wascontinued in combination with a 1 mg daily dose of lynestrenol [**52-76-6**] from day 91 for 10 days to ascertain whether secretory transformation of the endometrium and subsequent withdrawal bleeding would occur. Endometrial biopsies were obtained before treatment and on day 91. The effects of Org OD 14 on vaginal mucosa and cervical mucus were also

evaluated. Org OD 14 did not display any effect on the endometrium in 56 of the study subjects. Weak stimulation (initial proliferation was seen in 11 of the subjects, and withdrawal bleeding occurred in only 5 of these after cessation of the combined treatment with lynestrenol. However, moderate estrogenic effects on vaginal mucosa and cervical mucus were induced in all study subjects.

L5 ANSWER 7 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1976:577763 CAPLUS
DOCUMENT NUMBER: 85:177763
TITLE: Reactions in hyperacid media. XVIII. New synthesis of **7-methyl**-14-isoestranes
AUTHOR(S): Jacquesy, Jean C.; Jacquesy, Rose; Narbonne, Claudine
CORPORATE SOURCE: Lab. Chim. XII, Fac. Sci., Poitiers, Fr.
SOURCE: Bulletin de la Societe Chimique de France (1976), (7-8, Pt. 2), 1240-2
CODEN: BSCFAS; ISSN: 0037-8968
DOCUMENT TYPE: Journal
LANGUAGE: French
IT **14531-84-1**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with lithium dimethylcuprate)
RN 14531-84-1 CAPLUS
CN Estra-4,6-dien-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



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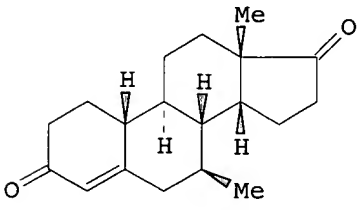


I

AB Treatment of androst-4-ene-3,17-dione with HF-SbF5 gave isoestrane I which resulted from either, a series of 1,2-migrations of the Me group or a 1,2-migration plus a 1,3-migration.

L5 ANSWER 8 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1974:27434 CAPLUS
DOCUMENT NUMBER: 80:27434

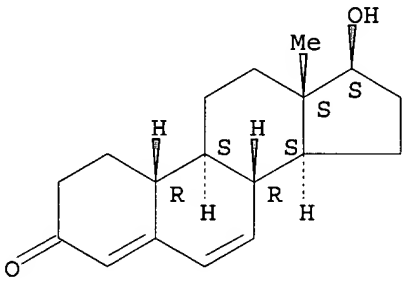
09937274

TITLE: 3-Oxo-7-alkyl-.DELTA.5-steroids
INVENTOR(S): Grunwell, Joyce F.; Benson, Harvey D.; Petrow, Vladimir
PATENT ASSIGNEE(S): Richardson-Merrell Inc.
SOURCE: Ger. Offen., 67 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2309328	A1	19731004	DE 1973-2309328	19730224
US 3833621	A	19740903	US 1972-236186	19720320
ZA 7300718	A	19731031	ZA 1973-718	19730131
AU 7351971	A1	19740808	AU 1973-51971	19730208
CA 1004667	A1	19770201	CA 1973-163914	19730216
GB 1416277	A	19751203	GB 1973-8774	19730222
NL 7302540	A	19730924	NL 1973-2540	19730223
CH 586236	A	19770331	CH 1973-3048	19730301
JP 49011870	A2	19740201	JP 1973-27642	19730310
BE 796909	A1	19730716	BE 1973-128910	19730316
SE 406591	C	19790531	SE 1973-3850	19730319
SE 406591	B	19790219		
FR 2181834	A1	19731207	FR 1973-9992	19730320

PRIORITY APPLN. INFO.: US 1972-236186 19720320
IT **14531-84-1**
RL: RCT (Reactant); RACT (Reactant or reagent)
(methylation of)
RN 14531-84-1 CAPLUS
CN Estra-4,6-dien-3-one, 17-hydroxy-, (17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



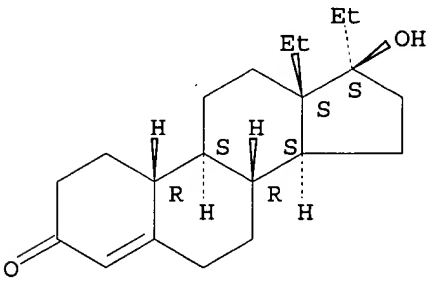
GI For diagram(s), see printed CA Issue.
AB Androstenones I (R =.alpha.-Me, .beta.-Me, .beta.-Me2CH; R1 = HO, AcO, EtCO2, Ac; R2 = H, Me, C.tplbond.CH; R1R2 = O, OCH2CH2O) (13 compds.), possessing anabolic, androgenic, progestational, and fertility inhibiting activity, were prepd. by reaction of LiR2Cu with the corresponding androstadienones II. Isomerization of I (R = .alpha.-Me, R1 = HO, R2 = H) with NaOMe in MeOH gave the corresponding .DELTA.4-isomer, which was used in treatment of prostate gland hypertrophy.

L5 ANSWER 9 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1968:419372 CAPLUS
DOCUMENT NUMBER: 69:19372

09937274

TITLE: Totally synthetic steroid hormones. XV. 6- and 7-Methylsteroids
AUTHOR(S): Buzby, G. C., Jr.; Douglas, G. H.; Walk, C. R.; Smith, H.
CORPORATE SOURCE: Wyeth Labs., Inc., Radnor, PA, USA
SOURCE: Proc. Int. Congr. Hormonal Steroids, 2nd, Milan (1967), Volume Date 1966 311-15
DOCUMENT TYPE: Journal
LANGUAGE: English
IT **1235-15-0**
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); BIOL (Biological study)
(biol. activity of)
RN 1235-15-0 CAPLUS
CN 18,19-Dinorpregn-4-en-3-one, 13-ethyl-17-hydroxy-, (17.alpha.)-(.+-.)-(9CI) (CA INDEX NAME)

Relative stereochemistry.



AB The prepn. of some 6- and 7-methylsteroids is described. m-Methoxyacetophenone was successively subjected to Reformatsky reaction with CH2BrCO2Me, hydrogenolysis, LiAlH4 redn., and reaction with PBr3 in C6H6 to give 3-(m-methoxyphenyl)butyl bromide. This compd. was subjected successively to reaction with NaC:CH in liq. NH3, Mannich condensation with CH2O and Et2NH, hydration, and distn. to give a mixt. of 7-(m-methoxyphenyl)-6-methylhept-1-en-3-one and 7-(m-methoxyphenyl)-6-methyl-1-diethylaminoheptan-3-one. This mixt. was condensed with 2-methylcyclopentane-1,3-dione to give the corresponding trione which underwent cyclodehydration in C6H6 contg. p-HO3SC6H4Me to give a mixt. of 6.alpha.- and 6.beta.-methyl-3-methoxyestra-1,3,5(10),8(9),14-pentaen-17-ones (I), in yields of 25 and 1%, resp. Similar condensation of the above ketone mixt. with 2-ethylcyclopentane-1, 3-dione followed by cyclodehydration gave a mixt. of 6.alpha.- and 6.beta.-methyl-3-methoxy-13-ethylgona-1,3,5 (10),8(9),14-pentaen-17-one, from which 6.beta.-methyl-3-methoxy-13-ethyl- 17-methylenedioxygona-1,3,5(10),8(9), 14-pentaene (II) was obtained in 40% yield. I and its 6.alpha.-isomer were subjected to successive hydrogenation, redn. with NaBH4, and Li-PhNH2 redn. to give 6.beta.- and 6.alpha.-methyl-3-methoxyestra-1,3,5(10)-triene-17-ols (III), resp. Hydrogenation, metal-NH3 redn., acid hydrolysis, and NaBH4 redn. of the ketal II gave 6.beta.-methyl- 3-methoxy-13.beta.-ethylgona-1,3,5 (10)-trien-17-ol (IV). III was also prepd. from 3-methoxyestra-1,3,5(10)-trien-17-ol by successive conversion to the acetate, oxidn., Grignard reaction with MeMgI, dehydration, and hydrogenation. IV was prepd. similarly from 3-methoxy-13-ethylgona-1,3,5(10)-trien-17-ol. 13.beta.-Ethyl-17.beta.-acetoxygona-4,6-dien-3-one (V) and 13.beta.,17.alpha.-diethyl-17.beta.-acetoxygona-4,6-dien-3-one (VI) were prepd. from the corresponding gon-4-en-3-ones. CuCl-Grignard

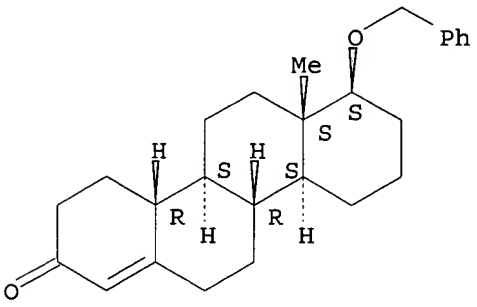
addn. with V gave 7.alpha.-methyl-13.beta.-ethyl-17.beta.-hydroxygon-4-en-3-one, while similar treatment of VI gave 7.alpha.-methyl-13.beta.,17.alpha.-diethyl-17.beta.-acetoxygon-4-en-3-one, which was converted by LiAlH4 redn. and subsequent MnO2 oxidn. to 13.beta.,17.alpha.-diethyl-17.beta.-hydroxygon-4-en-3-one. The biol. activity of some of the 6- and **7-methyl** steroids prepd. are tabulated.

L5 ANSWER 10 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1968:105442 CAPLUS
DOCUMENT NUMBER: 68:105442
TITLE: Tetracyclic compounds and methods of preparing the same
INVENTOR(S): Los, Marinus
PATENT ASSIGNEE(S): American Cyanamid Co.
SOURCE: U.S., 11 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3321489		19670523	US	19640604

IT **16154-55-5P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 16154-55-5 CAPLUS
CN D-Homoestr-4-en-3-one, 17a-(phenylmethoxy)-, (17a.beta.)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



AB 2-Ethylcyclohexane-1,3-dione (70 g.), 62 ml. Me vinyl ketone, 0.25 g. KOH, and 250 ml. abs. MeOH were refluxed together 4 hrs., MeOH and excess Me vinyl ketone distd. at atm. pressure, C6H6 added to the residue, distn. continued to 80.degree., C6H6 added to original vol., the soln. cooled in ice, 3 ml. pyrrolidine added, the H2O formed distd. azeotropically, the soln. cooled in ice, dild. with Et2O, and worked up to give 46.7 g. 1,6-dioxo-9-ethyl-.DELTA.5(10)-octalin (I), m. 67.5-8.5.degree. (ether-hexane), b0.6 130-5.degree.. NaBH4 (200 mg.) was added to 9.6 g. I in 90 ml. ice-cold abs. EtOH, after 15 min. another 200 mg. added, and after a second 15 min. period 160 mg. added, the soln. stirred an addnl. 15 min., acidified with glacial HOAc, and worked up to give 1-hydroxy-6-oxo-9-ethyl-.DELTA.5(10)-octalin (II) m. 88.0-9.5.degree.

(acetone-hexane), b0.8 165.degree.. II (3.98 g.), 10 ml. Ac2O, and 2 ml. C5H5N were heated on a steam bath 1.5 hrs., poured into 300 ml. ice H2O, and worked up to give 4.2 g. 1-acetoxy-6-oxo-9-ethyl-.DELTA.5(10)-octalin (III). III (44.4 g.), 44 ml. Et orthoformate, 4 ml. abs. EtOH, and 200 ml. C6H6 were mixed with 4 ml. abs. EtOH satd. with HCl, the mixt. refluxed 2 hrs., cooled, and worked up to give 1-acetoxy-6-ethoxy-9-methyl-.DELTA.4(10),5-hexahydronaphthalene (IV). IV was dissolved in 150 ml. abs. EtOH, hydrogenated at room temp. and pressure with 400 mg. 2% Pd-SrCO3 catalyst 2 hrs., and worked up to give 1-acetoxy-6-ethoxy-9-methyl-trans-.DELTA.6-octalin (V). V in 60 ml. 50% aq. HOAc was heated on a steam bath 0.5 hr. and worked up to give 4.1 g. 1-acetoxy-9-methyl-6-oxo-trans-decalin, m. 46-9.degree. (hexane). Prepd. similarly were: 4.7 g. 1-acetoxy-6-ethoxy-9-ethyl-.DELTA.4(10),5-hexahydronaphthalene; 4.7 g. 1-acetoxy-6-ethoxy-.DELTA.6-9-ethyl-trans-octalin; 4.1 g. 1-acetoxy-6-oxo-9-ethyl-trans-decalin; 74% 1-acetoxy-7-bromo-6-oxo-**9-methyl**-trans-decalin, m. 147-8.degree. (ether); 59% 1-acetoxy-6-oxo-9-methyl-.DELTA.7-trans-octalin, m. 62.5-3.5.degree. (ether-hexane); 10.2 g. 1-hydroxy-6-oxo-**9-methyl** -.DELTA.7-trans-octalin, m. 88-9.degree. (ether-hexane); 87% 1-tert-butoxy-6-oxo-9-methyl-.DELTA.7-trans-octalin, m. 72-3.degree.; 1-acetoxy-6,6-ethylenedioxy-9-methyl-trans-decalin, m. 116-17.degree.; 1-acetoxy-6,6-ethylenedioxy-9-ethyl-trans-decalin, m. 78.5-9.5.degree. (acetone-hexane); 84% 1-hydroxy-6,6-ethylenedioxy-9-methyl-trans-decalin, m. 71-2.degree.; 1-hydroxy-6,6-ethylenedioxy-9-ethyl-trans-decalin, m. 95-6.degree.; 13.0 g. 1-benzyloxy-6,6-ethylenedioxy-9-methyl-trans-decalin, m. 83.0-3.5.degree. (hexane), b0.5 176-82.degree.; 1-benzyloxy-6,6-ethylenedioxy-9-ethyl-trans-decalin, b0.5 182-4.degree.; 1-benzyloxy-6-oxo-9-methyl-trans-decalin, m. 46-7.degree. (hexane), b0.3 157.degree.; 1-benzyloxy-6-oxo-9-ethyl-trans-decalin; 51 g. 1-benzyloxy-7-bromo-6-oxo-methyl-trans-decalin, m. 112-13.degree. (acetone-hexane); 1-benzyloxy-7-bromo-6-oxo-9-ethyl-trans-decalin, m. 139-40.degree.; 1-benzyloxy-6-oxo-9-methyl-.DELTA.7-trans-octalin, b0.5 170.degree.; 1-benzyloxy-6-oxo-9-ethyl-.DELTA.7-trans-octalin, b0.1 165-70.degree.; 2.55 g. trans-1,2,4a,5,6,7,8,8a-octahydro-4a-methyl-5-tert-butoxy - 2-oxo - 1-naphthaldehyde; trans-1,2,4a,5,6,7,8,8a,-octahydro-4a-methyl - 5-benzyloxy-2-oxo-1-naphthaldehyde; trans-1,2,4a,5,6,7,8,8a-octahydro-4a-methyl-5-tert-butoxy-2-oxo-1-(3-oxobutyl(-1-naphthaldehyde; trans-1,2,4a,5,6,7,8,8a-octahydro-4a - methyl - 5-benzyloxy-2-oxo-1-(3-oxobutyl)-1-naphthaldehyde; trans - 1,2,4a,5,6,7,8,8a - octahydro-4a-methyl-5-benzyloxy-2-oxo - 1 -(3-oxopentyl-1-naphthaldehyde; Me trans-1-formyl-1,2,4a,5,6,7,8,8a-octahydro-4.alpha.-methyl-5-tert-butoxy-.delta.,2-dioxo-1-naphthaleneheptanoate; Me trans-1-formyl-1,2,4a,5,6,7,8,8a-octahydro-4a-methyl - 5- benzyloxy-.delta.,2-dioxo-1-naphthaleneheptanoate; dl-8.beta.-tert - butoxy-8a.beta.-methyl - 4,4a.beta.,4b.alpha.,5,6,7,8,8a-octahydro-2(3H)-phenanthrone, m. 134-5.degree. (ether-hexane); dl-8.beta.-benzyloxy-8a.beta.-methyl-4,4a.beta.,4b.alpha.,5,6,7,8,8a-octahydro-2(3H)-phenanthrone, m. 109-10.degree. (MeOH); dl-8.beta.-benzyloxy - 8a.beta.-1 - dimethyl - 4,4a.beta.4b.alpha.,5,6,7,8,8a, - octahydro-2(3H)-phenanthrone; dl-2,3,4,4a.beta.,4a.alpha.,5,6,7,8,8a-decahydro-8a.alpha.-methyl-8.beta.-tert-butoxy-2-oxophenanthrene-1-propionic acid, m. 88-9.degree. (MeCN); dl - 2,3,4,4a.beta.,4b.alpha.,5,6,7,8,8a,-decahydro-8a.beta.-methyl-8.beta.-benzyloxy-2-oxophenanthrene-1-propionic acid, m. 158-9.degree. (MeCN); dl-8.beta.-tert-butoxy-8a.beta.-methyl-4,4a.beta.,4b.alpha.,5,6,7,8,8a,9,10-decahydro-2(3H)-phenanthrone, m. 97-8.degree. (hexane); dl - 8.beta. - benzyloxy-8a.beta. - methyl - 4,4a.beta.,4b.alpha.,5,6,7,8,8a,9,10 - decahydro-2-(3H)-phenanthrone, m. 101-2.degree.; dl-8.beta.-benzyloxy-23,4,5a.beta.,4b.alpha.,5,6,7,8,8a,9,10-dodecahydro-8a.beta.-methyl - 2-oxo-phenanthrene-1-propionic acid; dl-17a.beta.-benzyloxy-5-hydroxy-3,5-

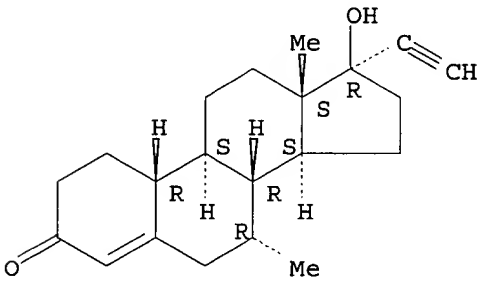
seco-4-nor-5(10),9(11)-D-homoestradien-3-oic acid, 3,5-lactone, m. 130-1.degree. (ether); dl-17a.beta.-benzyloxy-5-hydroxy-3,5-seco-4-nor-5(10)-D-homoestren-3-oic acid, 3,5-lactone, m. 123-4.degree. (ether-hexane); and dl-19-nor-D-homotestosterone, benzyl ether, m. 194-5.degree. (EtOH-CHCl3). Also claimed are: dl-17a.beta.-benzyloxy-13-ethyl-5-hydroxy-3,5-seco-4-nor-5(10),9(11)-D-homogonadien-3-oic acid, 3,5-lactone; dl-17a.beta.-tert-butoxy-5-hydroxy-3,5-seco-4-nor-5(10),9(11)-D-homoestradien-3-oic acid, 3,5-lactone; dl-17a.beta.-tert-butoxy-13-ethyl-5-hydroxy - 3,5-seco-4-nor-5(10),9(11)-D-homogonadien-3-oic acid, 3,5-lactone; dl-17a.beta.-tert-butoxy-5-hydroxy-3,5-seco-4-nor-5(10)-D-homoestren-3-oic acid, 3,5-lactone; dl-17a.beta.-benzyloxy-13-ethyl-5-hydroxy - 3,5-seco-4-nor-5(10)-D-homogonen-3-oic acid, 3,5-lactone; dl-17a.beta.-tert-butoxy-13-ethyl-5 - hydroxy-3, 5-seco - 4 - nor-5(10)- D - homogonen-3-oic acid, 3,5-lactone; dl-17.alpha.-benzyloxy-5-oxo-C-homoestr-4-ene; 17a.beta.-benzyloxy-13-ethyl-D-homogon-4-en-3-one.

L5 ANSWER 11 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1968:3127 CAPLUS
DOCUMENT NUMBER: 68:3127
TITLE: 7-Methyltestosterones
INVENTOR(S): Babcock, John C.; Campbell, J. Allan
PATENT ASSIGNEE(S): Upjohn Co., USA
SOURCE: U.S., 18 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 334155		19670912	US	19610605

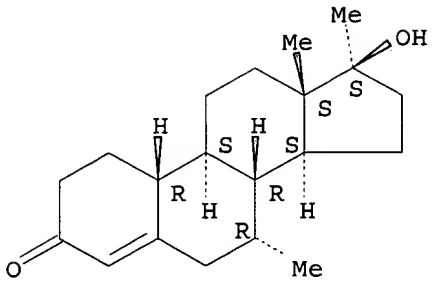
IT **1162-60-3P 3704-09-4P 3764-87-2P 6157-87-5P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 1162-60-3 CAPLUS
CN 19-Norpregn-4-en-20-yn-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.alpha.)-(9CI) (CA INDEX NAME)

Absolute stereochemistry.



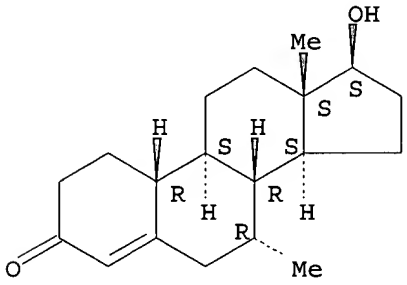
RN 3704-09-4 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-7,17-dimethyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



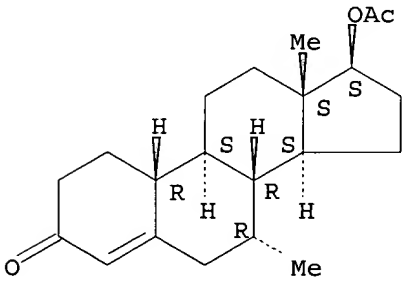
RN 3764-87-2 CAPLUS
CN Estr-4-en-3-one, 17-hydroxy-7-methyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 6157-87-5 CAPLUS
CN Estr-4-en-3-one, 17-(acetyloxy)-7-methyl-, (7.alpha.,17.beta.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



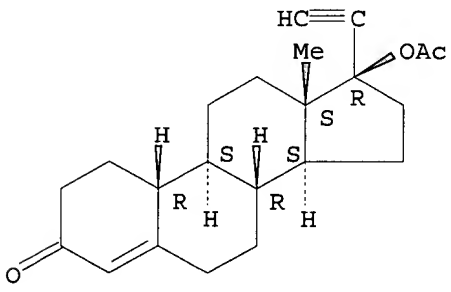
AB Compds. with anabolic, androgenic, antiestrogenic, gonadotropin-inhibiting, progestational, growth-promoting, anti-fertility, and central nervous system depressant activity were prepd. as follows. 11.beta.-Hydroxy-17.alpha.-methyltestosterone (5 g.) (CA 50: 7159b), 25 cc. Ac2O, and 100 mg. p-TsOH (Ts = tosyl) in toluene were refluxed under N 4.5 hrs., the product treated with NaBH4 3 days at 5.degree., followed by reaction with LiAlH4 gave 1.2 g. 17.alpha.-methyl-5-androstene-3.beta.,11.beta.,17.beta.-triol (I), m. 230-5.degree.; [.alpha.]D -68.degree. (dioxane). 11.alpha.-Hydroxy-17-methyltestosterone (1 g.) in pyridine was treated with 1 g. p-TsCl to give 11.alpha.-(p-

tolylsulfonyloxy)-17-methyltestosterone, which was refluxed with HCO2Na 19 hrs. to give 9(11)-dehydro-17-methyltestosterone. I (2 g.) and 12 g. p-quinone in PhMe was refluxed with 2 g. Al(OBu-tert)3 for 50 min. and chromatographed to give 0.4 g. 11.beta.-hydroxy-17.alpha.-methyl-6-dehydrotestosterone, m. 246-54.degree.; [.alpha.]D 150.degree. (CHCl3). Similarly prepd. were 6-dehydro-17-methyltestosterone (II), m. 182-91.degree.; [.alpha.]D 21.degree. (CHCl3). Using chloranil, 11.beta.-hydroxy-testosterone was converted to the 6-dehydro deriv. II (2 g.) was treated with a mixt. of 0.4 g. Cu2Cl2 and 20 cc. 4M MeMgBr in Et2O in tetrahydrofuran for 4 hrs. and the product chromatographed to give 1 g. of a mixt. of the 7-epimers of 7,17-dimethyltestosterone, m. 120-40.degree.; [.alpha.]D 55.degree. (CHCl3). Sepn. of the epimers was effected by recrystn. and reaction with chloranil to give the 7.alpha.-epimer, m. 163-5.degree., and the 7.beta.-epimer, m. 127-9.degree.. Similarly prepd. were the 7-epimers of 7,17-dimethyl-11.beta.-hydroxytestosterone, m. 218-24.degree., and sepn. as before gave the 7.beta.-epimer, m. 242-6.degree. (decompn.); [.alpha.]D 105.degree. (CHCl3); and by reaction with chloranil to give a residue, 7,17-dimethyl-11.beta.-hydroxy-6-dehydrotestosterone, m. 242-4.degree.; [.alpha.]D 310.degree. (CHCl3), and the 7.alpha.-epimer, m. 225-30.degree.; and 7.alpha.,17-dimethyl-9(11)-dehydrotestosterone, m. 172-6.degree. [obtained from 7.alpha.,17.alpha.-dimethyl-11.alpha.-hydroxytestosterone, m. 230-4.5.degree.; [.alpha.]D 81.degree. (CHCl3)]. 7.alpha.,17.alpha.-Dimethyltestosterone (8 g.), 8 g. Hg, 6.5 cc. HOAc, 5 g. SeO2, and 300 cc. tert-BuOH was refluxed under N for 4 hrs. to give, after chromatog., 1-dehydro-7.alpha.,17.alpha.-dimethyltestosterone, m. 153-6.degree.; [.alpha.]D -6.degree. (CHCl3). **7-Methyl**-11.beta.-hydroxytestosterone (III) (1 g.) was acetylated to give the 17-acetate. III (0.3 g.) in benzene was stirred with 0.3 cc. BzCl and 0.3 cc. pyridine for 17 hrs. at 25.degree. to give the 17-benzoate. This compd. (1.5 g.) in 80 cc. HOAc was oxidized with 0.74 g. CrO3 to give **7-methyl**-11-oxotestosterone 17-benzoate. Similarly prepd. was **7-methyl**-11-oxotestosterone 17-acetate. **7-Methyl**-11-oxotestosterone 17-propionate (1 g.) in 50 cc. N alc. KOH contg. 3 cc. H2O was refluxed 0.5 hr. to give **7-methyl**-11-oxotestosterone. III (2.5 g.), 250 cc. C6H6, 200 cc. Et2O, 100 cc. concd. HCl, and 100 cc. H2O was refluxed 18 hrs. to give 17-methyl-9(11)-dehydrotestosterone (IV). IV (250 mg.) in C6H6 was converted to the 17-propionate (V). Similarly prepd. was the 17-(.beta.-cyclopentyl-propionate) deriv. of IV. V (2 g.) in Me2CO was cooled to 15.degree. and treated with 2 g. N-bromoacetamide in H2O, followed by 10 cc. 0.8N HClO4 to give **7-methyl**-9.alpha.-bromo-11.beta.-hydroxytestosterone 17-propionate (VI). Similarly prepd. were **7-methyl**-9.alpha.-chloro-11.beta.-hydroxytestosterone 17-propionate, and 7,17-dimethyl 9.alpha.-bromo-11.beta.-hydroxytestosterone. VI (1.36 g.) in MeOH was titrated with 0.1N aq. NaOH to give **7-methyl**-9.beta.,11.beta.-epoxytestosterone 17-propionate (VII). Similarly prepd. was 7,17-dimethyl-9.beta.,11.beta.-epoxytestosterone. VII (1.13 g.) in CHCl3 was treated with HF in CHCl3 at -15.degree. to give **7-methyl**-9.alpha.-fluoro-11.beta.-hydroxytestosterone 17-propionate. This compd. (0.779 g.) in HOAc was treated with 0.37 g. CrO3 in HOAc to give **7-methyl**-9.alpha.-fluoro-11-oxotestosterone 17-propionate, which in turn was treated with alc. KOH to give **7-methyl**-9.alpha.-fluoro-11-oxotestosterone. 6-Dehydro-19-nortestosterone 17-acetate (3 g.) was treated with 3M MeMgBr and 0.4 g. Cu2Br2 to give 7.alpha.-methyl-19-nortestosterone 17-acetate, m. 111-14.degree.; [.alpha.]D 48.degree. (CHCl3). This product was deacetylated with aq. K2CO3 to give 7.alpha.-methyl-19-nortestosterone, m.

145-6.degree.; [.alpha.]D 55.degree. (CHCl3). This compd. (1.4 g.) was oxidized with CrO3 to give 7.alpha.-methyl-19-nor-4-androstene-3,17-dione, m. 201-4.degree.; and the product (10 mg.) in MeOH was treated with pyrrolidine to give 7.alpha.-methyl-19-nor-4-androstene-3,17-dione 3-pyrrolidinyl enamine (VIII), m. 151-60.degree.. VII (0.5 g.) was treated 5 hrs. with NaC.tplbond.CH in xylene to give 0.161 g. 7.alpha.-methyl-17.alpha.-ethynyl-19-nortestosterone (IX), m. 197-9.5.degree.. Also prepd. was the 17-acetate. IX was hydrogenated over Pd/C to give 17.alpha.-ethyl-7.alpha.-methyl-19-nortestosterone, m. 138-9.degree.. VIII (2.75 g.) was reacted with 3M MeMgBr to give 7.alpha.,17.alpha.-dimethyl-19-nortestosterone (X) which was then treated with Rhizopus nigricans ATCC 6227b to give 7.alpha.,17.alpha.-dimethyl-11.alpha.-hydroxy-19-nortestosterone (XI). X was similarly treated with Cunninghamella blakesleeana ATCC 8688b to give the 11.beta.-isomer of XI. CrO3-HOAc converted XI to 7.alpha.,17.alpha.-dimethyl-11-oxo-19-nortestosterone. To 1.6 g. 7.alpha.-methyl-11.beta.-hydroxy-19-nortestosterone in PhMe and cyclohexanone was added 1.5 g. Al(OBu-tert)3 to give 7.alpha.-methyl-11.beta.-hydroxy-19-nor-4-androstene-3,17-dione. 7.alpha.-Methyltestosterone (20 g.) was treated with 20 g. Na2Cr2O7 in HOAc to give 15.6 g. 7.alpha.-methyl-4-androstene-3,17-dione, m. 194-6.degree.; [.alpha.]D 196.degree. (CHCl3). The product was dissolved in hot MeOH and treated under N with pyrrolidine to give the 3-pyrrolidyl enamine, m. 199-205.degree. (decompn.); [.alpha.]D -190.degree. (pyridine). The compd. thus prepd. was treated with NaC.tplbond.CH as before to give 7.alpha.-methyl-17.alpha.-ethynyltestosterone, m. 191-3.degree.; [.alpha.]D 41.degree. (CHCl3). Hydrogenation converted the latter product to 7.alpha.-methyl-17.alpha.-ethyltestosterone, m. 140.5-3.0.degree.. This compd. was treated to give the 17-propionate. Uv and ir spectral data are given for the compds.

L5 ANSWER 12 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1965:14820 CAPLUS
DOCUMENT NUMBER: 62:14820
ORIGINAL REFERENCE NO.: 62:2665d-e
TITLE: March 1964 and corrections
AUTHOR(S): Anon.
SOURCE: Federal Register (1964), 29, 15228-9
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
IT **51-98-9**, 19-Nor-17.alpha.-pregn-4-en-20-yn-3-one, 17-hydroxy-, acetate
(approval of prepn. contg., for human use)
RN 51-98-9 CAPLUS
CN 19-Norpregn-4-en-20-yn-3-one, 17-(acetyloxy)-, (17.alpha.)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



AB The following new drugs have been approved for human use: ethynylestradiol and norethindrone acetate; aspirin, phenacetin, caffeine and orphenadrine citrate; norethindrone and mestranol; lidocaine, Bi subgallate, ZnO, Al subacetate, and Peruvian balsam; nalidixic acid; lidocaine; pralidoxime chloride; ammonium form of cross-linked polyacrylic (carboxylic) cation-exchange resin; and for veterinary use: trichlorfon, phenothiazine, and piperazine-di-HCl.

L5 ANSWER 13 OF 13 CAPLUS COPYRIGHT 2003 ACS
ACCESSION NUMBER: 1962:469431 CAPLUS
DOCUMENT NUMBER: 57:69431
ORIGINAL REFERENCE NO.: 57:13832d-i,13833a-i,13834a-i,13835a
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PATENT ASSIGNEE(S): Upjohn Co.
SOURCE: 83 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
BE 610385		19620516	BE	
DE 1182229			DE	
GB 941634			GB	
PRIORITY APPLN. INFO.:			US	19601116
			US	19610605

IT **1162-60-3**, 19-Nor-17.alpha.-pregn-4-en-20-yn-3-one, 17-hydroxy-7.alpha.-methyl- **3704-09-4**, Estr-4-en-3-one, 17.beta.-hydroxy-7.alpha.,17-dimethyl- **3764-87-2**, Estr-4-en-3-one, 17.beta.-hydroxy-7.alpha.-methyl- **6157-87-5**, Estr-4-en-3-one, 17.beta.-hydroxy-7.alpha.-methyl-, acetate (prepn. of)
RN 1162-60-3 CAPLUS
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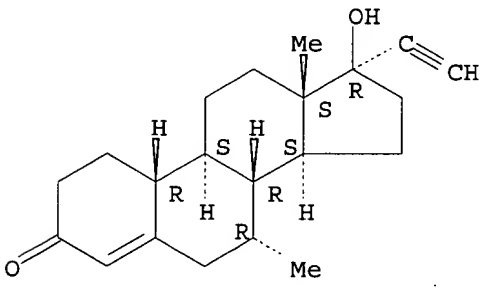
Absolute stereochemistry.



RN 3704-09-4 CAPLUS
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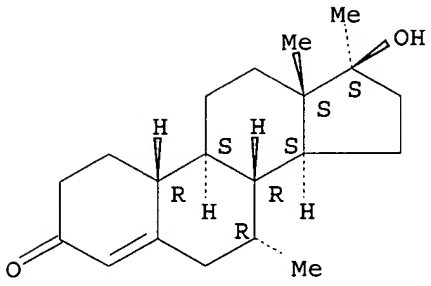
Absolute stereochemistry.



RN 3764-87-2 CAPLUS
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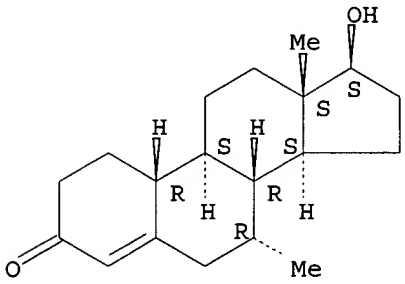
Absolute stereochemistry.



RN 6157-87-5 CAPLUS
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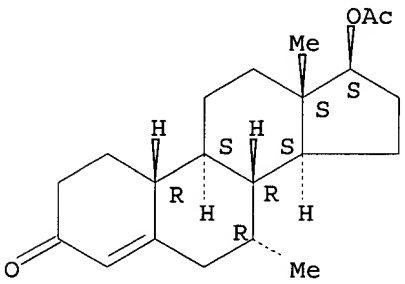
Absolute stereochemistry.



AB 11.beta.-Hydroxy-17.alpha.-methyltestosterone (I) (3 g.), 25 cc. Ac2O, and 100 mg. p-MeC6H4SO3H in 100 cc. MePh refluxed 4.5 hrs. under N and evapd., the residue dissolved in 100 cc. 95% EtOH, treated with 3 cc. 10% aq. NaOH, cooled to 0.degree., treated with stirring and cooling with 5 g. NaBH4 in 100 cc. 70% EtOH and after 1 hr. with an addnl. 2.5 g. NaBH4 in 50 cc. 70% EtOH, kept 3 days at 5.degree., heated to boiling with 15 cc. 10% aq. NaOH, and evapd., the residue treated with stirring with ice and 3N HCl and filtered, the washed and dried crude product (5.7 g.) dissolved in 50 cc. tetrahydrofuran, treated with stirring with 1.5 g. LiAlH4, dild. with 15 cc. Et2O, stirred 1 hr., and worked up yielded 1.7 g. 17.alpha.-methyl-5-androstene-3.beta.,11.beta.,17.beta.-triol (II), m.

230-5.degree. (EtOAc), [.alpha.]D -68.degree. (dioxane). 11.alpha.-Epimer of I (1 g.) in dry C5H5N treated 18 hrs. at room temp. with 1 g. p-MeC6H4SO2Cl and poured into H2O gave the 11.alpha.-(p-toluenesulfonate) (III). III (1 g.), 0.2 g. HCO2Na, 0.57 cc. H2O, and 14 cc. abs. EtOH refluxed 19 hrs., cooled, stirred into 50 g. ice and H2O, and filtered gave 9(11)-dehydro-17-methyltestosterone. II (2 g.), 12 g. p-benzoquinone, and 150 cc. MePh boiled to remove about 30 cc. MePh, treated with 2 g. (Me3CO)3Al, refluxed 50 min., cooled, washed with dil. aq. NaOH and H2O, and chromatographed on 100 g. Florisil yields 0.6 g. 11.beta.-hy droxy-17-methyl-6-dehydrotestosterone (IV), m. 246-54.degree. (EtOAc-Me2CO), [.alpha.]D 150.degree. (CHCl3). 17.alpha.-Methyl-5-androstene-3.beta.,17.beta.-diol (40 g.) and 170 g. p-benzoquinone in 1.3 I. MePh boiled to remove 250 cc. MePh, treated with 32 g. (Me3CO)3Al, refluxed 50 min., and worked up in the usual manner yielded 6.5 g. 6-dehydro-17-methyltestosterone (V), m. 182-91.degree. (hexane-Me2CO), [.alpha.]D 21.degree. (CHCl3). 11.beta.-Hydroxytestosterone (0.5 g.) in 50 cc. Me3COH refluxed under N with 0.5 g. chloranil during 2.5 hrs., concd. under a rapid N stream, dild. with CH2Cl2, and worked up, and the crude product chromatographed on Florisil gave 11.beta.-hydroxy-6-dehydrotestosterone. CuCl2 (0.4 g.), 20 cc. 4M MeMgBr in Et2O, and 60 cc. tetrahydrofuran treated with stirring and cooling with 2 g. V, 60 cc. tetrahydrofuran, and 0.2 g. CuCl2, stirred 4 hrs., decompd. with ice and H2O, acidified with 3N HCl, and extd. with Et2O, and the ext. chromatographed on 125 g. Florisil yielded 1 g. mixt., m. 120-40.degree., [.alpha.]D 55.degree. (CHCl3), of 7.alpha., 17-dimethyltestosterone (VI), m. 163-5.degree., and the 7.beta.-epimer, m. 127-9.degree.. VI (8 g.), 8 g. Hg, 6.5 cc. AcOH, and 5 g.SeO2 in 300 cc. Me3COH refluxed 4 hrs. with stirring, treated with 2 g. SeO2, refluxed an addnl. 3 hrs., concd. to about 200 cc. under a rapid stream of N, dild. with CH2Cl2 and Et2O, and worked up, and the crude product chromatographed on 200 g. Florisil gave 1-dehydro-7.alpha.,17.alpha.-dimethyltestosterone, m. 153-6.degree. (Me2COSkellysolve B), [.alpha.]D -6.degree. (CHCl3). CuCl2 (1.6 g.) in 240 cc. tetrahydrofuran and 100 cc. 3M MeMgBr in Et2O treated with 8 g. IV and 0.8 g. CuCl2 in 300 cc. tetrahydrofuran under N with stirring and cooling, and poured after 15 min. into Et2O, dil. HCl, and ice satd. with NaCl, the org. phase worked up, and the crude product chromatographed on 250 g. Florisil yielded 3.2 g. mixt., m. 218-24.degree. (hexane-Me2CO), [.alpha.]D 102.degree. (CHCl3), which by fractional recrystn. gave 7.beta., 17-dimethyl-11.beta.-hydroxytestosterone (VII), m. 242-6.degree. (decompn.) (Me2CO-MeOH), [.alpha.]D 105.degree. (CHCl3); a 0.5-g. portion of the mixt. (0.5 g.) in 50 cc. Me3COH treated 2.5 hrs. with 0.5 g. chloranil under N, concd. under a rapid stream of N, dild. with CH2Cl2, and worked up, and the crude product chromatographed on 100 g. Florisil yielded 100 mg. VII, m. 242-4.degree. (decompn.), [.alpha.]D 310.degree. (CHCl3), and 60 mg. 7.alpha.-epimer (VIII) of VII, m. 225-30.degree. with previous softening. 17-Methyl-6,9(11)-bisdehydrotestosterone gave similarly a mixt., m. 172-6.degree., of 7.alpha.- and 7.beta.-epimers of 7,17-dimethyl-9(11)-dehydrotestosterone, which is also obtained from 7.alpha.,-17.alpha.-dimethyl-11.alpha.-hydroxytosterone, m. 230-43.5.degree., [.alpha.]D 81.degree. (CHCl3), via the 11.alpha.-(p-toluenesulfonate) with HCO2Na in aq. EtOH. 7-**Methyl**-11.beta.-hydroxytestosterone (IX) (1 g.) in 6 cc. dry C5H5N and 6 cc. Ac2O kept 17 hrs., poured onto ice, and filtered gave the 17-acetate (X). IX (0.3 g.) in 12 cc. dry C6H6 treated with 0.3 g. BzCl and 0.3 cc. dry C6H6 gave similarly the 17-benzoate (XI) of IX. XI (1.5 g.) in 80 cc. AcOH treated with 0.74 g. CrO3 in 4 cc. H2O and 80 cc. AcOH, kept 5 hrs. at room temp., treated with 10 cc. MeOH, and evapd., and the residue triturated with H2O and extd. with Et2O yielded 7-**methyl**-11-oxotestosterone 17-benzoate. X was oxidized similarly

to **7-methyl**-11-oxotestosterone 17-acetate. 17-Propionate (1 g.) of **7-methyl**-11-oxotestosterone (XII) in 50 cc. N KOH-MeOH contg. 3 cc. H2O refluxed 0.5 hr., poured onto ice, neutralized with dil. H2SO4, and filtered gave XII. IX (2.5 g.), 250 cc. C6H6, 200 cc. Et2O, 100 cc. concd. HCl, and 100 cc. H2O refluxed 18 hrs. with stirring, and the org. layer worked up yielded **7-methyl**-9(11)-dehydratestosterone (XII). XIII (250 mg.) in 30 cc. C6H6 heated to remove 18 cc. C6H6, cooled, treated with 2 cc. C5H5N and 2 cc. (EtCO)2O, kept 22 hrs. at about 26.degree., dild. with 25 cc. H2O, and extd. with Et2O gave the 17-propionate (XIV) of XIII. XIII (250 mg.) in C6H6 gave in the same manner with 0.25 cc. B-cyclopentylpropionyl chloride the 17-(.beta.-cyclopentylpropionate) of XIII. XIV (2 g.) in 100 cc. Me2CO cooled to 15.degree., treated with 2 g. AcNHBr in 50 cc. H2O, kept at 12.degree., treated with 10 cc. 0.8N HClO4 and after 5 min. with an addnl. 10 cc. HClO4 followed after a further 10 min. by 20 cc. HClO4, treated after 20 min. with satd. aq. Na2SO3, dild. with 200 cc. H2O, and filtered gave **7-methyl**-9.alpha.-bromo-11.beta.-hydroxytestosterone 17-propionate (XV). XIV (1 g.) in 50 cc. Me3COH treated at 20-5.degree. with 1 g. N-chlorosuccinimide in Me3COH and 50 cc. 0.1N H2SO4, stirred 0.5 hr. at room temp., dild. with 300 cc. H2O, and extd. with CH2Cl2 gave **7-methyl**-9.alpha.-chloro-11.beta.-hydroxytestosterone 17-propionate. 7,17-Dimethyl-9(11)-dehydrotestosterone (XVI) (1 g.) in 50 cc. dioxane treated at 24.degree. with 1 g. N-bromosuccinimide in 50 cc. dioxane and then during 1 hr. at room temp. with 50 cc. 0.1N H2SO4, dild. with 300 cc. H2O, and extd. with CH2Cl2 gave 7,17-dimethyl-9.alpha.-bromo-11.beta.-hydroxytestos-terone. XV (1.36 g.) in 50 cc. MeOH titrated against phenolphthalein with 0.1N aq. NaOH, dild. slowly with stirring with 300 cc. H2O, cooled, and filtered gave **7-methyl**-9.beta.,11.beta.-epoxytestosterone 17-propionate (XVII). XVII (1.13 g.) in 20 cc. CHCl3 added with cooling to HF in CHCl3 in a polyethylene bottle, kept 4 hrs. at 15.degree., and poured into excess satd. aq. NaHCO3, the CHCl3 phase worked up, and the crude product chromatographed on 100 g. Florisil gave the 9.alpha.-F analog (XVIII) of XV. XVIII (0.779 g.) in 40 cc. AcOH treated with 0.37 g. CrO3 in 2 cc. H2O and 40 cc. AcOH, kept 5 hrs. at room temp., treated with 10 cc. MeOH, dild. with 200 cc. H2O, and extd. with Et2O, and the ext. worked up gave **7-methyl**-9.alpha.-fluoro-11-oxotestosterone 17-propionate (XIX). XIX (0.5 g.) and 80 mg. KOH in 10 cc. EtOH and 1 cc. H2O heated 1 hr. on the water bath, poured into 50 cc. H2O, neutralized with dil. HCl, and extd. with CH2Cl2 gave **7-methyl**-9.alpha.-fluoro-11-oxotestosterone. 17-Acetate analog (1 g.) of XVIII in O-free MeOH treated at 18-20 under N with 1 g. KHCO3 in 10 cc. O-free H2O, stirred 20 hrs. at room temp., neutralized with iced dil. AcOH, concd. to about 60 cc., and refrigerated 16 hrs. yielded 7 **-methyl**-9.alpha.-fluoro-11.beta.-hydroxytestosterone. MeMgBr (3M) in 25 cc. Et2O and then 0.4 g. CuBr2 added with stirring and cooling under N to 30 cc. tetrahydrofuran, the mixt. treated with 3 g. 6-dehydro-19-nortestosterone 17acetate in 50 cc. tetrahydrofuran, stirred 10 min. with cooling, and poured into iced dil. HCl satd. with NaCl, the org. phase worked up, the residue treated 18 hrs. at room temp. with 5 cc. C5H5N and 5 cc. Ac2O, and the crude product chromatographed on Florisil gave an oil which rechroma-tographed on 30 g. 2:1 Celite-Darco gave 1 g. 17-acetate (XX) of 7.alpha.-methyl-19-nortestosterone (XXI), m. 111-14.degree. (MeOH), [.alpha.]D 48.degree. (CHCl3). XX (3 g.) in 40 cc. 5% K2CO3-80% aq. MeOH refluxed 2 hrs. under N and extd. with Et2O) gave XXI, m. 145-6.degree., [.alpha.]D 55.degree. (CHCl3). CrO3 (1.4 g.) in 15 cc. C5H5N treated with stirring and cooling with 1.4 g. XXI in 15 cc. C5H5N, stirred 20 hrs. at about 20.degree., dild. with 1:1 C6H6-Et2O, filtered through Celite, and extd. gave 1.4 g. 7.alpha.-methyl-19-

norandrostene-3,17-dione (XXII), m. 201-4.degree. (Me2CO), lambda; 239.5 m.mu. (.epsilon. 17,000). XXII (10 mg.) in a little boiling MeOH treated with 1 drop pyrrolidine, concd., and refrigerated gave the 3-pyrrolidinyl enamine (XXIII) of XXII, m. 151-60.degree., .lambda. 282 m.mu. (e 23,450). C2HNa (20% suspension in xylene) (1 cc.) centrifuged, the residue suspended in 6 cc. Me2SO, treated with XXIII from 0.5 g. XXII, kept 5 hrs. at room temp. under N, treated dropwise with H2O, dild. with 2 cc. H2O and 5 cc. MeOH, heated 1 hr. on the water bath, and extd. with Et2O gave 0.161 g. 7.alpha.-methyl-17.alpha.-ethynyl-19-nortestosterone (XXIV), m. 1979 2O-Skellysolve B), 240.5 m.mu.. XXIV (100 mg.) hydrogenated over 30 mg. prehydrogenated 1% Pd-C in 20 cc. dioxane until 2 equivs. H had been absorbed, filtered through Celite, and evapd., and the residue combined with the same product from 50 mg. XXIV, dissolved in CHCl3, and chromatographed on 50 g. Florisil gave the 17.alpha.-Et deriv. of XXI, m. 138-9.degree. (Skellysolve B-Et2O), .alpha. 241 m.mu. (.epsilon. 17,000). XXIII (2.75 g.) in 70 cc. tetrahydrofuran added with stirring under N to 25 cc. 2M MeMgBr in Et2O, the mixt. distd. to 55.degree. vapor temp., the residue refluxed 4 hrs. and worked up in the usual manner, and the crude product chromatographed on 100 g. Florisil gave the 17.alpha.-Me deriv. (XXV) of XXI. XXV (2 g.) in 20 cc. HCONMe2 added to 10 l. of a 24-hr. Rhizopus nigricans (ATCC 6227b) culture in 2% aq. corn steep liquor contg. 1% dextrose, incubated 72 hrs. and extd. with CH2Cl2, and the residue from the ext. chromatographed on Florisil gave 7.alpha., 17.alpha.-dimethyl-11.alpha.-hydroxy-19-nortestosterone (XXVI). XXV (0.2 g.) in 30 cc. EtOH added to 1 l. 48-hr. Cunninghamella blakesleeana culture incubated 48 hrs. and extd. with 3:1 CH2Cl2-EtOAc, and the residue chromatographed on Florisil yielded the 11.beta.-epimer of XXVI. XXVI (1.5 g.) in 80 cc. AcOH treated 5 hrs. at room temp. with 0.74 g. CrO3 in 4 cc. H2O and 80 cc. AcOH and worked up in the usual manner yielded the cryst. 7.alpha.,17.alpha.-dimethyl-11- oxo-19-nortestosterone. 7.alpha.-Methyl-11.beta.-hydroxy-19-nortestosterone (1.6 g.) in 35 cc. MePh and 15 cc. cyclohexanone heated to remove about 10 cc. solvent, treated with 1.5 g. (Me3CO)3Al, refluxed until the reaction was complete, treated with excess satd. aq. NaK tartrate, and steam distd. to remove the solvents, the distn. residue extd. with CH2Cl2, and the residue from the ext. chromatographed on Florisil yielded 7.alpha.-methyl-11.beta.-hydroxy-19-norandrostene-3,17-dione (XXVII). XXIV (1 g.), 20 cc. Ac2O, and 1 cc. C5H5N heated 1 hr. with stirring under N at 140.degree., cooled to room temp., stirred 2 hrs. with 100 cc. H2O, and filtered gave a mixt. of the 17-acetate (XXVIII) of XXIV and the corresponding 3-enol 3,17-diacetate; the mixt. refluxed 1 hr. with 100 cc. MeOH contg. 2 cc. concd. HCl, dild. with H2O, and extd. with Et2O, and the residue from the ext. chromatographed on Florisil gave the cryst. XXVIII. Na2Cr2O7.2H2O (20 g.) in 200 cc. AcOH treated with stirring and cooling with 20 g. 7.alpha.-methyltestosterone, kept several hrs. at room temp., poured into 1 l. H2O, and filtered gave 18.7 g. 7.alpha.-methylandrostene-3,17-dione (XXIX), m. 194-6.degree. (Me2CO-Skellysolve B), [.alpha.]D 196.degree. (CHCl3), .lambda. 241 m.mu. (.epsilon. 17,250). XXIX (15.6 g.) in the min. amt. boiling MeOH under N treated with 10 cc. pyrrolidine, cooled, and filtered gave the 3-pyrrolidinyl enamine (XXX) of XXIX, m. 199-205.degree. (decompn.), [.alpha.]D - 190.degree. (C5H5N), .lambda. 282 m.mu. (.epsilon. 29,900). C2HNa centrifuged from 25 cc. 20% suspension in xylene, resus pended in 160 cc. Me2SO, treated with the XXX in 100 cc. Me2SO, stirred 3 hrs. under N, treated with 30 cc. H2O and 50 cc. MeOH, heated 1 hr. at 50-60.degree., kept at room temp. overnight, dild. with H2O, and extd. with CH2Cl2, the ext. worked up, and the crude product (2 g.) combined with 3.9 g. product from the filtrate and chromatographed on DarcoCelite-Florisil gave 3.9 g. 7.alpha.-methyl-17.alpha.-ethynyltestosterone (XXXI), m. 191-3.degree. (EtOAc), [.alpha.]D

41.degree. (CHCl3), .lambda. 242 m.mu. (.epsilon. 16,550). XXXI (1 g.) hydrogenated over 0.2 g. prehydrogenated 1% Pd-C in 40 cc. dioxane yielded 0.8 g. 17.alpha.-Et analog (XXXII) of XXXI, m. 140.5-43.degree., .lambda. 242 m.mu. (e 16,350). XXXII (5 g.) in 20 cc. C5H5N and 5 cc. (EtCO)2O refluxed under N gave the 17-propionate of XXXII. XXXI (5 g.) in 20 cc. C5H5N and 5 cc. (EtCO)2O gave similarly the 17-propinnate of XXXI.

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=> s l8 and 7-alkyl
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         500431 ALKYL
           1966 7-ALKYL
                  (7(W)ALKYL)
L9            0 L8 AND 7-ALKYL

=> s l8 and 7-ethyl
        2305927 7
         330054 ETHYL
           1319 7-ETHYL
                  (7(W)ETHYL)
L10           0 L8 AND 7-ETHYL

=> s l8 and 7-methyl
        2305927 7
         778688 METHYL
           6873 7-METHYL
                  (7(W)METHYL)
L11           0 L8 AND 7-METHYL

=> d his

     (FILE 'HOME' ENTERED AT 12:37:05 ON 25 JAN 2003)

     FILE 'REGISTRY' ENTERED AT 12:37:38 ON 25 JAN 2003
L1            0 S 19-NIR TESTOSTERONE
L2          162 S 19-NOR TESTOSTERONE
L3            0 S L2 AND 7-SUBSTITUTED

     FILE 'CAPLUS' ENTERED AT 12:38:52 ON 25 JAN 2003
L4            3 S L2 AND 7-ALKYL
L5           13 S L2 AND 7 METHYL
L6            0 S L2 AND 7ETHYL
L7            1 S L2 AND 7 ETHYL
L8          540 S NANDROLONE
L9            0 S L8 AND 7-ALKYL
L10           0 S L8 AND 7-ETHYL
L11           0 S L8 AND 7-METHYL

=> s l2 and 7-vinyl
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         351185 VINYL
            323 7-VINYL
                  (7(W)VINYL)
L12           0 L2 AND 7-VINYL
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09937274

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=> s l2 and 7-alkylene
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       2305927 7
         50070 ALKYLENE
           270 7-ALKYLENE
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L13          0 L2 AND 7-ALKYLENE

=> S l2 and 7-alpha ethyl
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       2305927 7
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        330054 ETHYL
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L14          0 L2 AND 7-ALPHA ETHYL
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09937274

AND CURRENT DISCOVER FILE IS DATED 01 OCTOBER 2002
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FILE 'HOME' ENTERED AT 14:36:45 ON 25 JAN 2003

=> file reg
COST IN U.S. DOLLARS SINCE FILE ENTRY TOTAL SESSION
FULL ESTIMATED COST 0.21 0.21

FILE 'REGISTRY' ENTERED AT 14:36:51 ON 25 JAN 2003
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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

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Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details:
http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

=> s 95171-22-5/rn
L1 1 95171-22-5/RN

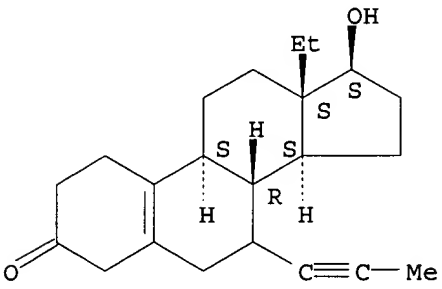
=> d l1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2003 ACS
RN **95171-22-5** REGISTRY
CN Gon-5(10)-en-3-one, 13-ethyl-17.beta.-hydroxy-7-(1-propynyl)- (7CI) (CA

09937274

INDEX NAME)
FS STEREOSEARCH
MF C22 H30 O2
LC STN Files: CAOLD

Absolute stereochemistry.



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

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ALL L# QUERIES AND ANSWER SETS ARE DELETED AT LOGOFF
LOGOFF? (Y)/N/HOLD:H

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	2.48	2.69

SESSION WILL BE HELD FOR 60 MINUTES
STN INTERNATIONAL SESSION SUSPENDED AT 14:37:47 ON 25 JAN 2003